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Bridgman growth of detached GeSi crystals

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Abstract

$Ge_{1-x}Si_x$ ($0<x<0.12$) has been grown by the vertical Bridgman technique using adjustments in the applied temperature profile to control the pressure difference between the bottom and top of the melt. Using this technique, a pressure difference is created by decreasing the temperature in the gas volume above the melt while the sample is molten but prior to growth. A maximum pressure difference approximately equal to the hydrostatic pressure of the molten sample can thus be obtained. Several GeSi crystals were grown in pyrolitic boron nitride ampoules. When a pressure difference was applied, samples were reproducibly grown mostly detached. For comparison, samples were also grown in a configuration in which gas could flow freely between the gap below the melt and the volume above the melt and no pressure difference could be established. These samples were initially attached. Existence of detachment was determined both by measuring the surface roughness of the samples with a profilometer and by observations of the sample surfaces with optical and electron microscopy. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Numerous authors have reported results of Bridgman growth experiments in which crystals appear to have grown with little or no contact with the ampoule wall. These occurrences are observed more frequently among semiconductor crystals grown under microgravity conditions [1]. Features observed include bubbles or voids along the ampoule wall, gaps of between 1 and 60 μm between the ingot and the ampoule, and necking behavior with gap widths of up to several millimeters. In the detached regions, facets and waves and bands normal to the axis were sometimes observed. Understanding the mechanisms leading to detachment is driven, in part, by the improved quality of such crystals. For example, CdZnTe grown without wall contact in microgravity exhibited virtually no twinning and a 100× reduction in dislocation density [2].

The mechanisms which give rise to detachment are not completely understood, although there are several parameters that are expected to potentially play a role. Rough interior crucible surfaces [3], large contact angles, large growth angles, and a small melt-gas surface tension have been predicted

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to promote detachment [4,5]. Another key parameter, and one which is the subject of this paper, is the difference in pressure between the top and bottom of the melt. During detached Bridgman growth, the melt is in contact with the crucible wall but the crystal is not. A meniscus exists at the bottom of the melt between the crucible and crystal. The pressure in the gap region below the melt, relative to the pressure above the melt, is expected to influence the shape of the meniscus and the existence and stability of detachment [4,6].

Duffar et al. [7] conducted a stability analysis to determine the conditions for the detached growth of InSb in SiO_2. They found that stable detached growth was possible but that a pressure difference close to the hydrostatic pressure must be maintained throughout the growth process. Thus, the pressure difference needed to be continuously controlled and lowered during growth as the melt height and hydrostatic pressure continuously decreased. They also conducted an experiment in which the pressure above and below the melt was actively controlled by connecting these volumes to gas sources. Using this technique, a 41 mm region of detached GaSb was grown. However, significant problems related to oxygen contamination were noted. More recently, Duffar et al. [8] improved on this technique by eliminating the necessity of external gas sources. This was done by using an ampoule with an inert gas reservoir below the seed. This gas volume was heated independently of the Bridgman furnace to control the pressure of the gas below the melt.

Wilcox and Regel [9] proposed another mechanism by which a pressure difference could be initiated and maintained; rejection of a volatile impurity at the crystal-melt interface and liberation of the volatile impurity at the meniscus and into the gap region. Although this mechanism might explain previous detached growth results, it would be difficult to intentionally implement and control. It would require, at a minimum, knowledge of the solubility of dissolved gases in the melt and knowledge and control of both the distribution and transport of these gases in the melt.

In this work, we describe a technique by which adjustments in the applied temperature profile are used to control the pressure difference between the bottom and top of the melt. It is similar in concept to that recently reported by Duffar et al. [8]. However, instead of having a heated gas volume below the sample, this technique induced a pressure difference by reducing the temperature of the gas volume above the melt. A maximum pressure difference approximately equal to the hydrostatic pressure of the molten sample can be obtained. If the pressure difference becomes larger, gas will bubble through the melt until a pressure difference equal to the hydrostatic pressure is established. In a microgravity environment, the pressure difference is not limited by the hydrostatic head, and a larger pressure difference can be induced. This is a possible reason why crystals grown in space are sometimes detached from the crucible wall. The technique eliminates the possibility of sample contamination that can occur if the crucible is connected to external gas sources [7]. Experimental results of the growth of GeSi by this technique are presented. For comparison, GeSi was also grown in a configuration in which gas could flow between the gap below the melt and the volume above the melt such that no pressure difference could be established.

2. Experimental

A series of 12 mm diameter GeSi samples were grown to assess the influence of applied pressure differences on detachment. The starting material consisted of a Ge seed with Ge and Si ingots placed on top. The stochiometry resulted in a melt with nominally 2 at% Si concentration. After etching, the starting material was loaded into pyrolitic boron nitride (pBN) ampoules. In one ampoule configuration, the pBN liner was open on both ends, and the sample was supported on a graphite pedestal with a hole in the center. The hole in the pedestal prevented pressure from building up below the meniscus. Other ampoules were closed on the bottom so that any gas below the melt would be trapped there. The ampoules were placed inside an outer SiO_2 ampoule which was filled with 600 mbar Ar containing 2% H_2 and then sealed. Growth experiments were conducted

in resistively heated furnaces with seven separately controllable zone heaters.

A schematic drawing of the ampoule configurations and the applied temperature profiles is shown in Fig. 1. Initially, the furnace was heated to a typical Bridgman temperature profile. Four thermocouples were affixed to the outside of the SiO_2. The typical axial temperature gradient at the crystal-melt interface, as measured by the thermocouples, was $\sim 35\,K/cm$. The furnace was slowly lowered down over the samples until $\sim 20\,mm$ of Ge starting material remained as a seed. For the closed ampoule configuration, the temperatures of the top zones of the furnace were then lowered to obtain profile 2 in Fig. 1. The decrease in temperature resulted in a decreased pressure in the volume above the melt. Calculations indicate that the imposed change in pressure was larger than the hydrostatic pressure of the melt. Therefore, it is expected that bubbling occurred and that the pressure difference established prior to growth was approximately equal to the hydrostatic pressure plus any pressure resulting from surface tension. For the open ampoule configuration, the top furnace zone temperatures were not lowered. If the bottom were closed, a pressure difference could occur if dissolved gases in the melt preferentially evolved at the meniscus [9]. Therefore, ampoules were open on the bottom to insure that no pressure difference could be established across the melt. After the furnace was lowered, the GeSi melt was allowed to homogenize for several hours. The samples were grown with furnace translation velocities between 0.2 and 0.3 μm/s.

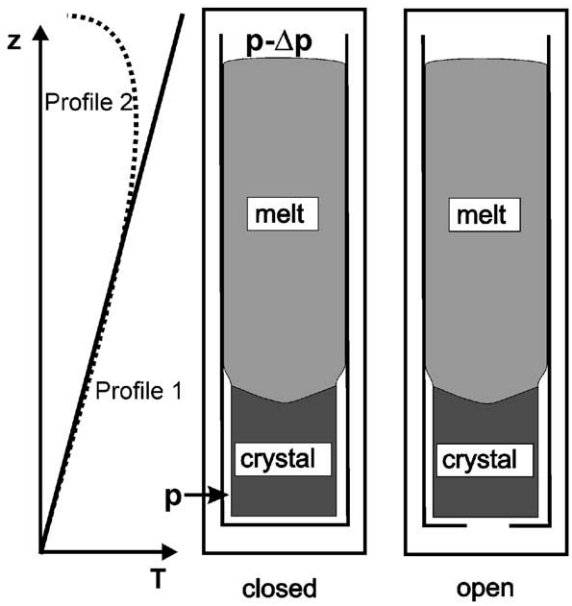

Fig. 1. Schematic drawing of the technique. A pressure difference is induced in the closed ampoule configuration when the temperature above the melt is lowered (profile 2).

3. Results and discussion

Several crystals were grown in both ampoule configurations. Although all crystals slid out of the pBN ampoules quite easily after growth, the crystals grown in the open ampoules always contained large areas of attachment, while those grown in the closed ampoule configuration were detached over most of the length of the crystal. The extent of attachment or detachment was ascertained by measuring the surface roughness with a stylus type profilometer and by microscopic observations of surface features.

Fig. 2 shows results typical of a sample grown in a closed ampoule using the retrograde temperature profile technique described in the previous section. The profilometer measurement shows several key features that occurred during the growth process. The increase in the profilometer measurement at 3 mm shows the change in sample diameter at the meltback interface. After the meltback interface, there is a region of free growth that occurs during the homogenization period as the Si is incorporated into the molten Ge [10]. The Si dissolves into the molten Ge and is transferred to the crystal melt interface by diffusion and/or convection. Crystal growth occurs without furnace translation until the Si concentration in the solid is in equilibrium with the Si concentration in the melt, as determined by the Ge–Si equilibrium phase diagram [11,12]. The beginning of a smooth band at approximately 18 mm marks the end of the free growth period, and the start of furnace translation. As evidenced by the profilometer measurements, the sample surface is quite rough up to the 35 mm position and then becomes smooth. The cause and

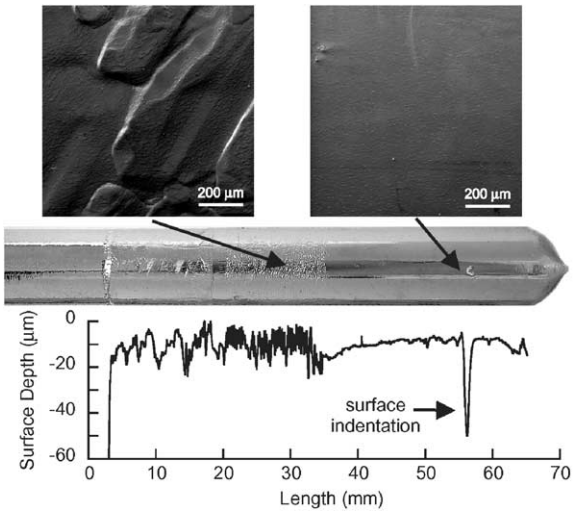

Fig. 2. A closed ampoule configuration result. The secondary electron images give expanded views of rough and smooth sample regions. The *x*-axis dimensions of the profilometer measurements also correspond to the dimensions of the macroscopic picture.

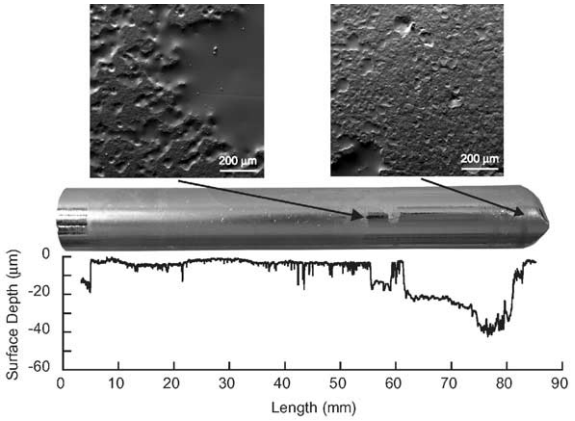

Fig. 3. An open ampoule configuration result. The left-hand secondary electron image is an expanded view of the transition between attached and detached regions. The right-hand image is an expanded view of a completely attached region. The *x*-axis dimensions of the profilometer measurements also correspond to the dimensions of the macroscopic picture.

effect relationship between the sample roughness, the crystallinity at the surface, and the stability of the interface are currently under investigation. The authors consider this sample almost completely detached, although there are a few areas ($<1\,mm^2$) of attachment in the rough surface regions.

Fig. 3 shows one of the samples grown in an open ampoule configuration with surface features characteristic of attached growth. The attached regions have a hazy appearance and are readily distinguished from the detached regions, which are relatively shiny. In this sample, there is a smaller difference between the seed crystal and ampoule at the meltback interface because the sample fit more tightly into the ampoule than the sample shown in Fig. 2. The expanded left-hand image in Fig. 3 shows the transition from attachment to detachment and the right-hand image shows a nearly completely attached region near the very end of the sample. It is not at present clear why detachment occurs at about 55 mm. It is possible that a circumferential region of attachment may provide a pressure seal. If so, then any evolved gas at the crystal-melt interface would increase the pressure below the melt. This mechanism, in combination with the reduced hydrostatic pressure near the end of the sample, may be the cause of the detachment.

In conclusion, adjustments in the applied temperature profile have been successfully used to induce a gas pressure below the melt larger than that above it. GeSi was reproducibly grown mostly detached using this technique. When a pressure difference was prevented from being established, GeSi was reproducibly grown attached. In several instances it was observed that initially attached samples became detached towards the end of growth. Built-up pressure from evolved gas at the melt-crystal interface, as described by Wilcox and Regel [9], in combination with the reduced hydrostatic pressure towards the end of growth, may account for this phenomenon. Differences in structural quality between attached and detached regions will be reported in a separate article.

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